Munitions Constituents Sampling

Closed Castner Firing Range

Fort Bliss, TX

TPP Meeting

20 October 2010

Agenda

- Defining the Problem
- Project Objectives
- Project Goals
- Where do we plan to sample?
- How do we plan to sample?
- Schedule & Questions

Defining the Problem

- Castner Range is a large site (7,007 acres)
- Varied types of firing ranges and munitions types used from 1930s – 1960s
- Heterogeneous distribution of munitions constituents (MC).
- How to determine presence/absence of MC?
- If presence of MC, how to determine nature and extent of contamination?
- Unknown future land use

Many MMRP Sites around the country have the same problems.

The Problem: Heterogeneous Chunks (Chips)

- Heterogeneous:
  - Put 10 chips into a cookie recipe
  - Bake 100 cookies
  - Majority of cookies (samples) will have zero chips (underestimating chocolate concentration)
- Homogeneous:
  - Try it again but, this time, grind and blend the dough until the chocolate is evenly distributed throughout
  - Every cookie (sample) will have a representative amount of chocolate (makes really bad cookies though)

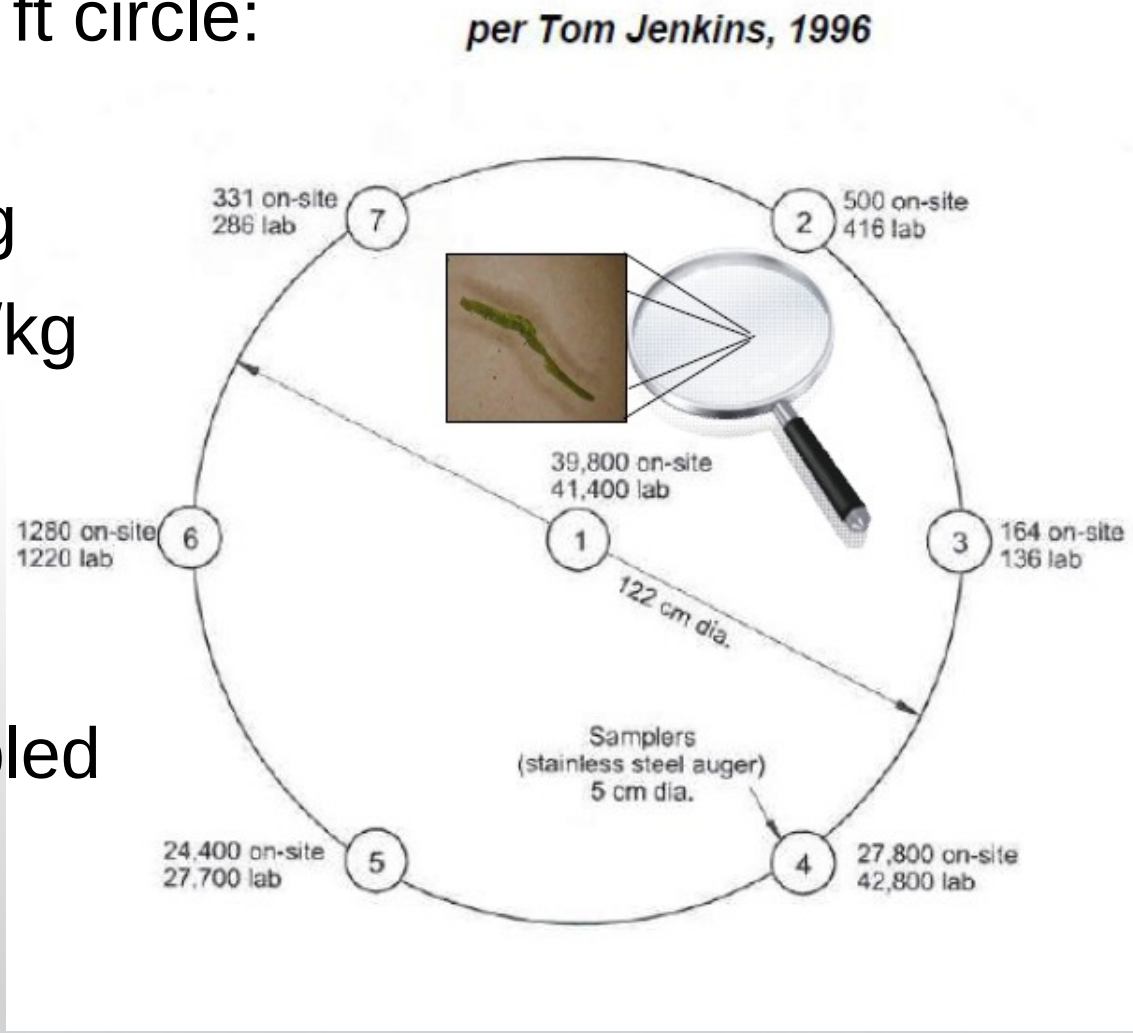
Munitions Constituents (MC)

- Energetics (examples):
  - Nitramines (RDX)
  - Nitroaromatics (TNT)
  - Nitrate Esters (NG)
- Metals (examples):
  - Lead
  - Antimony
  - Zinc
  - Copper

Heterogeneity of Explosives in Soils

14 Samples from a 4 ft circle:

- Range from
  136 – 42,800 ug/kg
- Mean = 14,900 ug/kg
- Median = 1,220
- Relative Standard Deviation = 120%
- 1.2% of area sampled



Project Goals

- Implement and test the effectiveness of the Army's Incremental (MI) Sampling Protocol on the Closed Castner Firing Range, Fort Bliss, TX
- Gain regulatory acceptance of MI sampling approach and results
- Characterize MC at Castner Range (will not be 100%)
- Test some hypotheses about the MI sampling approach on Castner Range

Study Objectives

- Collect data in a manner that allows for use under Texas Commission on Environmental Quality (TCEQ) Texas Risk Reduction Program (TRRP)
- Determine presence or absence of munitions constituents (MC) (energetics and metals)
  - If presence of MC, then determine nature and extent through comparison to TRRP Protective Concentration Levels (PCLs)
- TCEQ accept sampling results for use in future investigation and remediation efforts
  - Using Texas Accredited Laboratory
  - Validating Data in accordance with TCEQ TRRP guidance document, TRRP-13 *Review and Reporting of Chemicals of Concern (COC) Concentration Data*

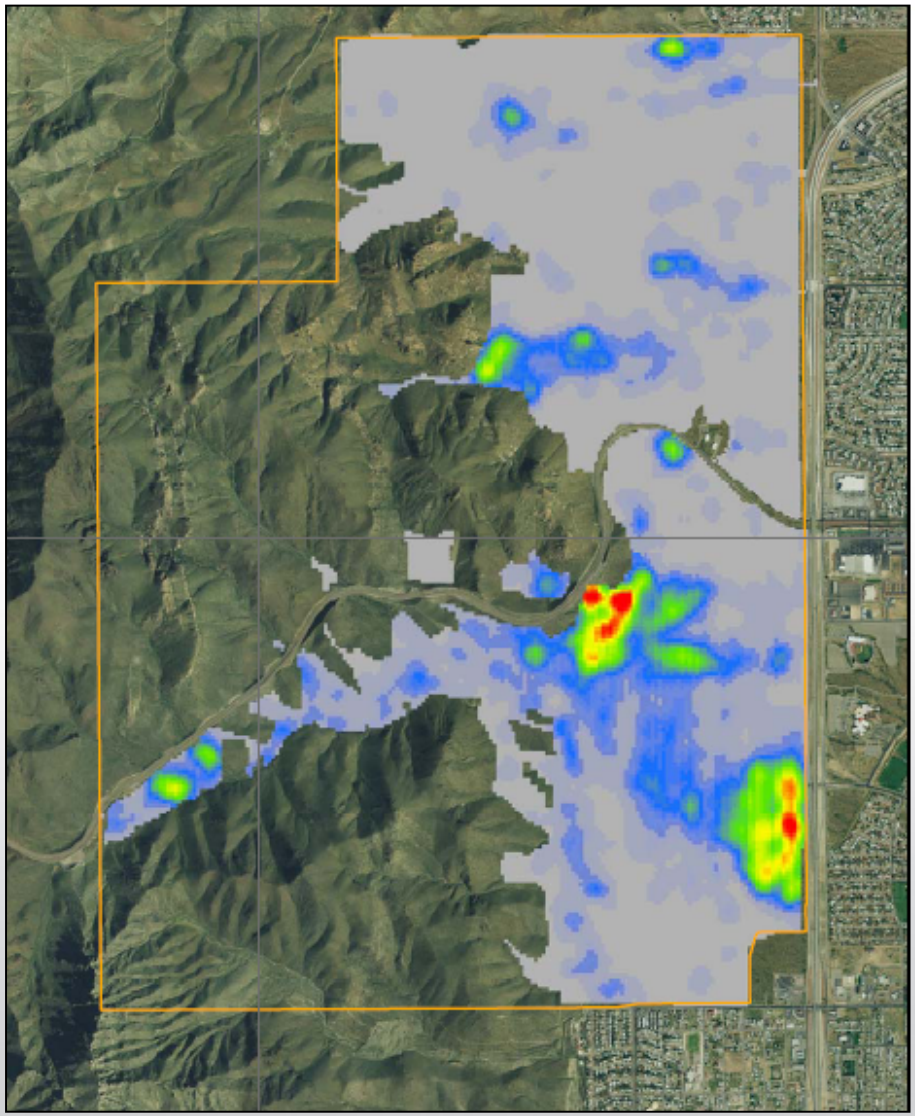
Proposed Study Questions

1. How to determine presence or absence of MC using a representative concentration approach?
2. Are MC present on Castner Range? If so, are they above regulatory concentrations?
3. What is the effect of sampling unit size on MI sampling results (MC concentrations)?
4. What is the correlation between Munitions and Explosives of Concern (MEC) and Munitions Debris (MD) density on MC concentrations?
5. What modifications to the Army MI Sampling Guidance would make implementation more effective and efficient in the context of an Military Munitions Response Program (MMRP) Remedial Investigation (RI)?

Sampling Strategy

- Determine Sampling Design
  - random sampling, biased sampling, stratified sampling, systematic sampling
- Identify Sampling Units (number and size)
- Determine appropriate PCLs and ecological benchmarks for metals
- Implement Army's Incremental Sampling Protocol and EPA Analytical Methods (8330B and 6010B)
- Use data to determine nature and extent of contamination

Sampling Area



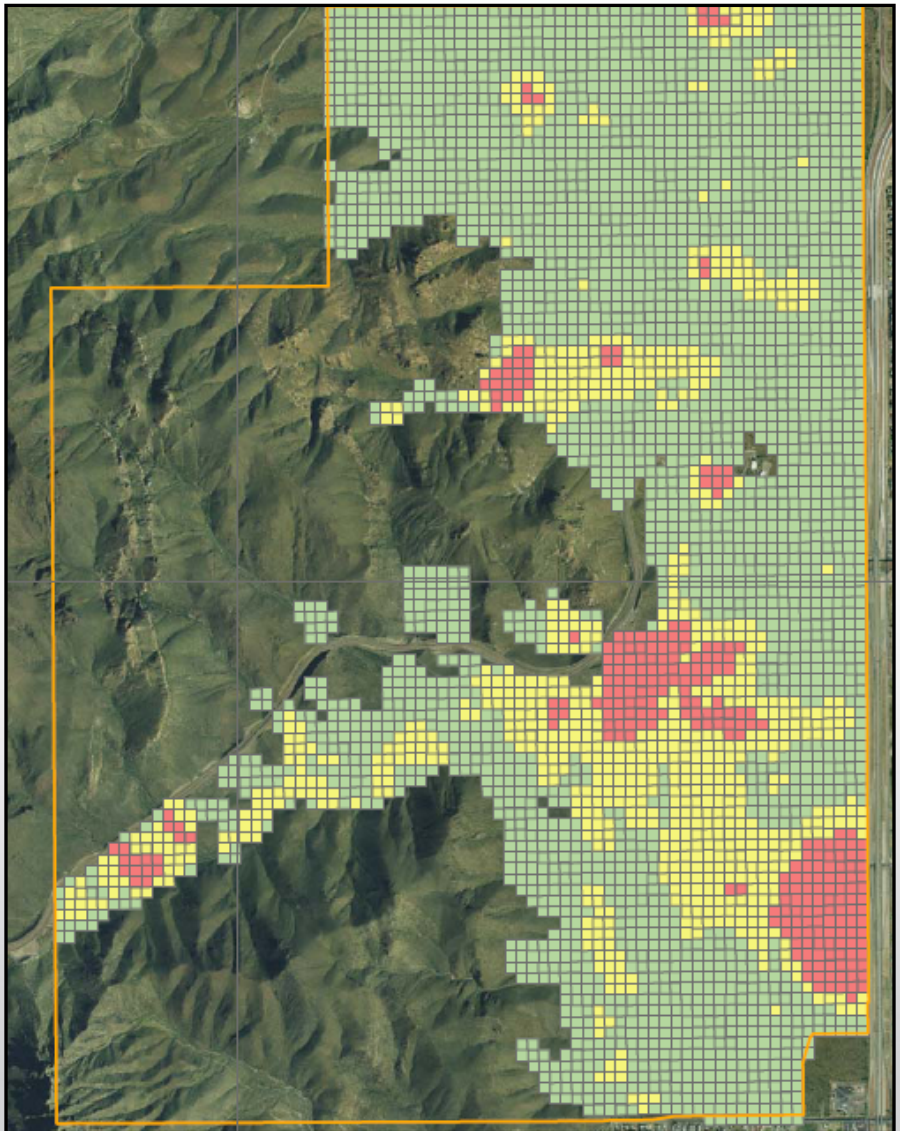
Sampling Area Design

Stratify site into “like areas” using previously collected geophysical data

- Low anomaly densities (unlikely to find MC): 0 - 300 anomalies per acre
- Medium anomaly densities (may find MC): 300 - 700 anomalies per acre
- High anomaly densities (likely to find MC): >700 anomalies per acre

Stratifying site increases validity of “homogeneity” assumption. Increases power of random samples. Increases accuracy of estimates. Answers study question #4.

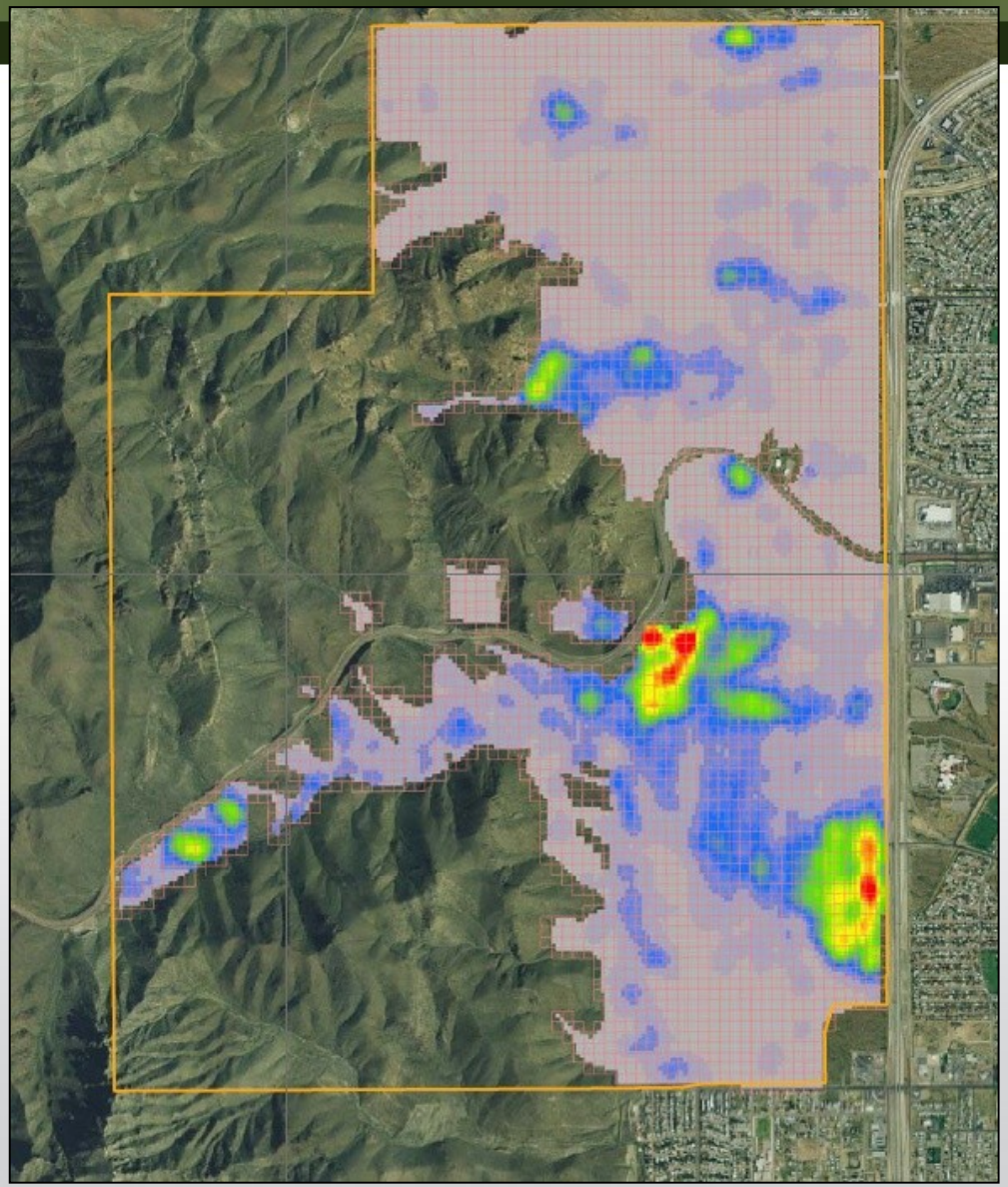
Stratified Sampling Area



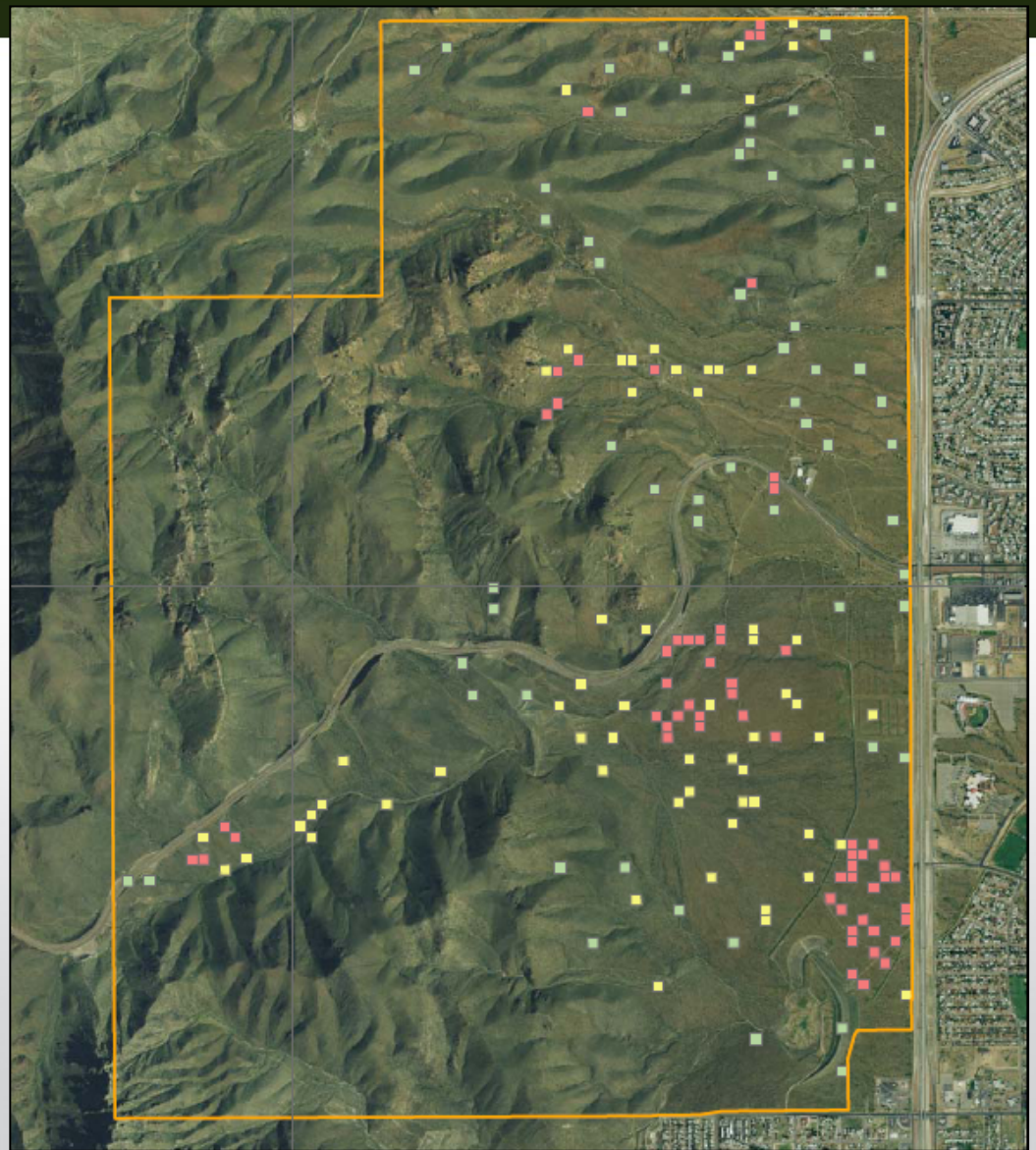
Creating Sampling Units

- Divided the accessible areas into 1-acre sampling units
  - Approximately 3,700 possible sampling units
- Randomly select 60 1-acre sampling units within each strata
  - Low areas: 60 samples
  - Medium areas: 60 samples
  - High areas: 60 samples
- Approach allows us to draw conclusions, with 95% confidence, that the sample results are representative of all the 1-acre sampling units within each strata (high, medium, & low)
  - If no “detects” of MC in a strata, we are 95% confident there will be no detects of MC in at least 95% of the remaining of 1-acre parcels in that strata.
  - If mean concentration of samples is X, we can be 95% confident that the actual mean concentration of all units within a strata is within ±2 standard errors of X.

Sampling Units

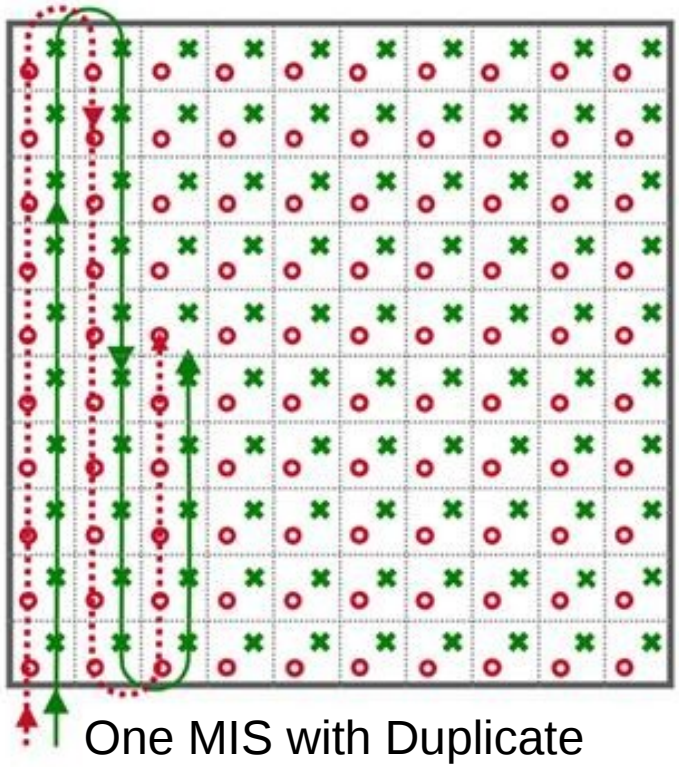


Stratified Sampling Units



Sampling Effort #1

- Take a 100-increment sample within each selected 1-acre sampling unit
  - 60 samples in low areas
  - 60 samples in med areas
  - 60 samples in high areas
- 10% Sample Replicates (triplicates)
- Shallow surface soils (5cm)
- Uniform sample depth
- Uniform sample size



One MIS with Duplicate

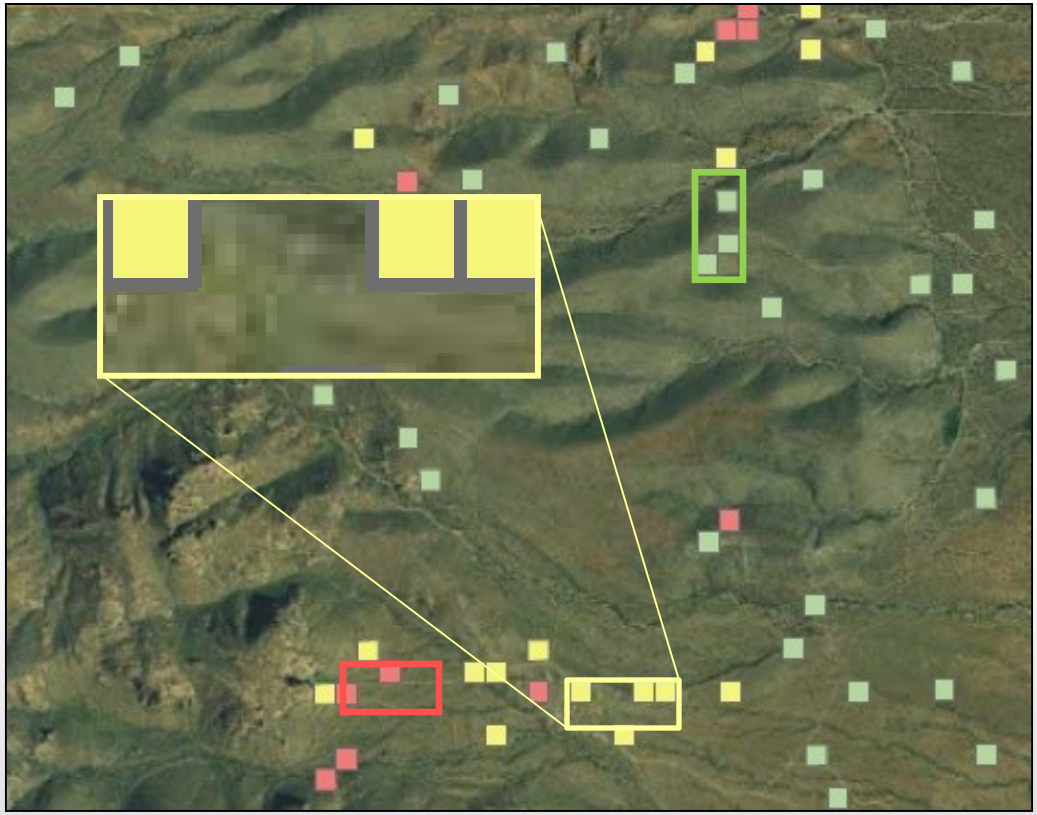
Determines presence or absence of MC within each 1-acre sampling unit, within each strata, and within the site. Also, provides insight into nature and extent of MC.

Sampling Effort #2

- A research effort to test sensitivity of sampling unit size on MI sampling results (MC concentrations)
- Two approaches (still a work in progress and likely to change):
  1. Sample 10-acre sampling units that include previously sampled 1-acre units.
  2. Create “virtual” 10-acre sampling units incorporating 10 previously sampled 1-acre units.

Sampling Effort #2: Approach 1

- Create 10-acre sampling unit including previously sampled 1-acre units
- Sample 15, 10-acre units
  - 5 in “low” areas
  - 5 in “medium” areas
  - 5 in “high” areas
- Take 10 increments per each 1-acre unit to make 100 increments per 10-acre samp

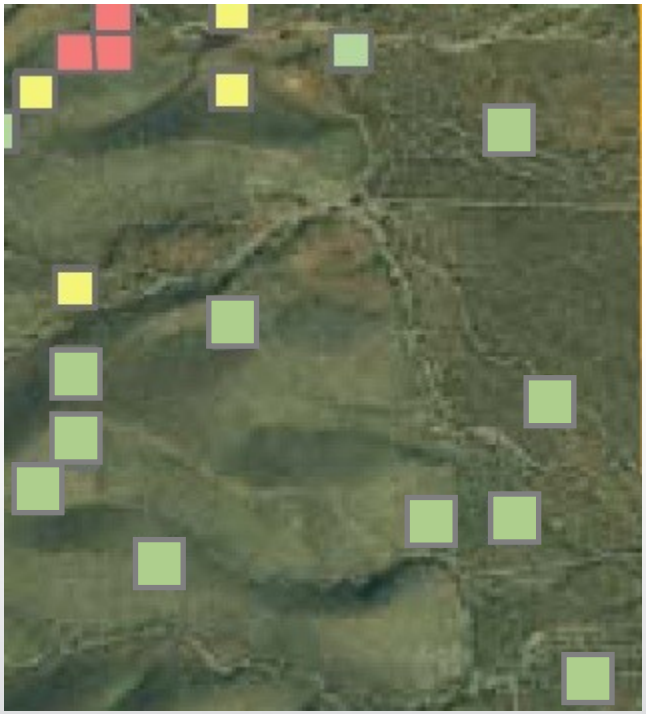


Pros: Allows us to draw conclusions about contiguous areas.
Cons: Introduces variability associated with sampling units previously not sampled. (Not purely a test of the effect of sample unit size.)

URS

Sampling Effort #2: Approach 2

- Use previously studied 1-acre sampling units
- Create 15, virtual 10-acre sampling units
  - 5 in “low” areas
  - 5 in “medium” areas
  - 5 in “high” areas
- Take 10 increments per each 1-acre unit to make 100 increments per 10-acre sampling unit



Pros: Pure test of the effect of sample unit size on MIS results.
Cons: Does not allow us to draw conclusions about contiguous areas.

Sampling Tools

- Sandy soil with lots of rock
- Looking for tool ergonomically sound, standard size, & fast
- Testing tools tomorrow (21 Oct 2010)

Laboratory Analysis

- Sampling for presence/absence of energetics and metals
  - EPA Method 8330B (explosives)
  - EPA Method 6010B (metals)
- Using TX Accredited Laboratory

Analyte	Analytic Method
EXPLOSIVES	
Amino-2,6-dinitrotoluene, 4-	SW846 8330B
Amino-4,6-dinitrotoluene, 2-	SW846 8330B
Cyclotetramethylenetetranitramine (HMX)	SW846 8330B
Cyclotrimethylenetrinitramine (RDX)	SW846 8330B
Dinitrobenzene, 1,3- (dinitrobenzene, 2,4-)	SW846 8330B
Dinitrotoluene, 2,4- (2,4-DNT)	SW846 8330B
Dinitrotoluene, 2,6- (2,6-DNT)	SW846 8330B
Trinitrobenzene, 1,3,5- (TNB)	SW846 8330B
Trinitrophenylmethylnitramine (tetryl; nitramine)	SW846 8330B
Trinitrotoluene, 2,4,6- (TNT)	SW846 8330B
METALS	
Aluminum	SW846 6010B
Antimony	SW846 6010B
Arsenic	SW846 6010B
Barium	SW846 6010B
Beryllium	SW846 6010B
Cadmium	SW846 6010B
Chromium (total)	SW846 6010B
Cobalt	SW846 6010B
Copper	SW846 6010B
Lead (inorganic)	SW846 6010B
Manganese	SW846 6010B
Mercury (pH = 4.9)[6]	SW846 7471A
Nickel and compounds	SW846 6010B
Selenium	SW846 6010B
Silver	SW846 6010B
Thallium and compounds (as thallium chloride)	SW846 6010B
Tin	SW846 6010B
Vanadium	SW846 6010B
Zinc	SW846 6010B

Data Screening

To define nature and extent, analytical results will be screened against the most current (March 2010) Protective Concentration Levels (PCLs)

- Data initially screened against Tier 1 Residential PCLs for 30-acre source area (most conservative)
- Select PCLs in accordance with TRRP using the lower of the:
  - $^{Tot}Soil_{Comb}$: Protective of the Total Soil Combined exposure pathway (includes direct contact with soils, ingestion of soils)
  - $^{GW}Soil_{Ing:}$ Protective of pathway for leaching of soil contaminants to groundwater (assumes a Class 1 or 2 groundwater)
  - $^{Air}Soil_{Inh-v}$: Protective of the inhalation of contaminants in soil volatilizing into the air exposure pathway.
  - For metals, compare value to background. If background higher, use background in lieu of TRRP PCLs.
- Data, if detected concentrations exceed PCLs, will be compared to ecological benchmarks

Data Screening: What does this mean?

- We are going to compare our results two ways:
  - Against TCEQ established levels (Protective Concentration Levels (PCLs)) including background for metals
  - Ecological benchmarks if we have detections
- If sampling results for individual sampling units exceed PCLs and/or background, review historical information and evaluate magnitude of exceedance before drawing conclusions.

TCEQ PCL Screening Levels

Chemical of Concern	CAS	30 acre source area							Texas-Specific Background (mg/kg)
		$^{Tot}Soil_{Comb}$[2]		$^{GW}Soil_{Ing}$			$Air Soil_{Inh-V}$[4]		
		(mg/kg)	note3	(mg/kg)	note3		(mg/kg)	note3	
EXPLOSIVES									
Amino-2,6-dinitrotoluene, 4-	19406-51-0	8.9E+00	n	3.3E-02	n		4.5E+01	n	
Amino-4,6-dinitrotoluene, 2-	35572-78-2	9.3E+00	n	5.0E-02	n		5.6E+01	n	--
Cyclotetramethylenetetranitramine (HMX)	2691-41-0	2.0E+02	n	1.2E+00	n		2.3E+02	n	--
Cyclotrimethylenetrinitramine (RDX)	121-82-4	2.5E+01	n	1.8E-02	c		2.9E+01	n	--
Dinitrobenzene, 1,3- (dinitrobenzene, 2,4-)	99-65-0	6.3E+00	n	3.8E-03	n		1.2E+02	n	--
Dinitrotoluene, 2,4-	121-14-2	6.9E+00	c	2.7E-03	c		1.5E+01	n	--
Dinitrotoluene, 2,6-	606-20-2	6.9E+00	c	2.4E-03	c		2.2E+01	n	--
Nitrobenzene	98-95-3	3.4E+01	c	1.8E-01	n		3.4E+01	c	--
Nitrotoluene, m-	99-08-1	2.7E+02	n	9.2E-01	n		4.5E+02	n	--
Nitrotoluene, o-	88-72-2	2.1E+01	c	1.6E-02	c		4.9E+02	n	--
Nitrotoluene, p-	99-99-0	1.7E+02	n	2.2E-01	c		4.4E+02	n	--
Trinitrobenzene, 1,3,5-	99-35-4	2.0E+03	n	9.1E-01	n				--
Trinitrophenylmethylnitramine (tetryl; nitramine)	479-45-8	3.4E+01	n	5.5E-01	n		3.9E+01	n	--
Trinitrotoluene, 2,4,6-	118-96-7	1.7E+01	n	8.6E-02	n		3.7E+01	n	--
METALS									
Aluminum	7429-90-5	6.4E+04	n	8.6E+04	n	>S			30000
Antimony	7440-36-0	1.5E+01	n	2.7E+00	m	>S			1
Arsenic	7440-38-2	2.4E+01	n	2.5E+00	m	>S			5.9
Barium	7440-39-3	7.8E+03	n	2.2E+02	m	>S			300
Beryllium	7440-41-7	3.8E+01	n	9.2E-01	m	>S			1.5
Cadmium	7440-43-9	5.2E+01	n	7.5E-01	m	>S			0.574
Chromium (total)	7440-47-3	2.7E+04	n	1.2E+03	m	>S			30
Cobalt	7440-48-4	2.1E+01	n	3.3E+00	n	>S			7
Copper	7440-50-8	5.5E+02	n	5.2E+02	a	>S			15
Lead (inorganic)	7439-92-1	5.0E+02	n	1.5E+00	a	>S			15
Manganese	7439-96-5	3.4E+03	n	5.8E+02	n	>S			300
Mercury (pH =4.9)[6]	7439-97-6	2.1E+00	n	3.9E-03	m		2.4E+00	n	0.748
Nickel and compounds	7440-02-0	8.3E+02	n	7.9E+01	n	>S			10
Selenium	7782-49-2	3.1E+02	n	1.1E+00	m	>S			0.3
Silver	7440-22-4	9.5E+01	n	2.4E-01	n	>S			--
Thallium and compounds (as thallium chloride)	7791-12-0	6.3E+00	n	8.7E-01	m				9.3
Tin	7440-31-5	3.5E+04	n	1.8E+04	n	>S			0.9
Vanadium	7440-62-2	2.9E+00	n	1.7E+01	n	>S			50
Zinc	7440-66-6	9.9E+03	n	1.2E+03	n	>S			30

Schedule & Way Ahead

- October – November 2010: Develop Work Plan and Quality Assurance Project Plan
  - Sampling Approach
  - Laboratory Standard Operating Procedures
  - Data Validation Procedures
- February 2011: Soil Sampling
- March – May 2011: Analytical testing and report writing

Questions